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THE HISTORY OF CHEMISTRY—II.

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DEVELOPMENT OF ORGANIC CHEMISTRY IN THE LAST FIFTY YEARS

THE science of organic chemistry developed, as we have seen, very slowly until consistent ideas as to the mode of combination of the elements, and consequently as to the structure of compounds, were established; but since then its growth has been by leaps and bounds. To-day the organic chemist has prepared, described, and ascertained the constitution of compounds numbering 150,000 or more; amongst these, in addition to a large number which had previously been isolated from natural products, are a vast number never known until built up in the laboratory. Indeed as soon as he established the structural principles upon which organic compounds are built up, he became an architect and designer of chemical structures, using as units the radicles or groups, and proceeded in his laboratory to learn how to build up such structures. And so it is now possible to synthesize in the laboratory a relatively complex substance such as uric acid from its elements; or, starting from benzene or napthalene, the chemist may finish with a dye-stuff, a regular skyscraper of a compound whose structural formula fills half a page and whose systematic name requires several lines of type in more than one font.

In this connection it may be remarked that the so-called coal-tar or aniline dyes bear about the same relation to coal-tar or aniline as a steel battleship does to a heap of iron ore, the latter being merely the raw material from which the former is fashioned. Moreover, an artificial or synthetic substance is no imitation or substitute, but is the real thing and indeed is often purer and better than the natural product; synthetic indigo is real indigo, a synthetic ruby is a real ruby, the only difference being that one is produced by what we are pleased to call natural processes, whereas in the other the process is controlled so as to yield a pure product.

The successful synthesis of a substance is usually not possible until its structure has been established, a matter which may require long-continued laborious effort and analysis; even then it may be realized very slowly, for one must learn how to make his units combine to form the structure desired. Successful synthesis in the laboratory does not imply that this synthesis will directly be carried out on a large scale;

the development of an economically feasible scheme of operations requires a time measured in years rather than in months—even in wartime, when considerations of financial economy are secondary and when more effective co-operation can be secured, the interval between preparation by the gram and production by the ton is a matter of many months. Indeed in some cases—e. g., sugar and rubber—there is no immediate prospect of synthetic production on any large scale, because the material can be built up in the growing plant—the sugar cane or the rubber tree—at a cost comparable with that of the basic raw material required in its artificial production.

The story of even a single achievement in synthesis would be so long and would involve so many technical details and explanations that it cannot be given here; we shall have to limit ourselves to a mention of some of the outstanding examples, premising that these achievements became possible only because of knowledge slowly accumulated by the efforts of many men possessed by a curiosity with respect to the inwardness of things.

Aniline, discovered first in 1840 as a decomposition product of indigo, was found in coal-tar by Hofmann in 1843; in 1845, after his discovery of benzene in coal-tar, Hofmann could make aniline in large quantities from benzene. In 1856 Perkin, a student of Hofmann, while oxidizing some crude aniline, obtained a dye; this was mauve, the first of the aniline dyes, the starting-point of an industry which has since grown to enormous proportions. In 1868 alizarin, hitherto prepared from madder root, was synthesized, and, within a few years, was being made on a large scale, to the complete displacement of the natural product. Indigo was prepared first in 1870, made from accessible coal-tar derivatives in 1880, but it was not until 1890 that the process was discovered which ultimately proved successful commercially; about 1902 the synthetic indigo came on the world-market, and by 1914 Germany was selling over a million pounds a month at about fifteen cents a pound, as compared with a price four times as great ten years earlier. This list of materials made from coal-tar derivatives could be extended indefinitely to include a whole host of compounds, many of which were not known at all until built up by the chemist, used as dyes or drugs, antiseptics or anaesthetics, perfumes or flavors, and now indeed considered indispensable.

About a hundred years ago, Biot observed that a ray of light polarized in one plane has that plane twisted in passing through certain organic substances; and that the direction and extent of this rotation of the plane of polarization is different for different substances. In 1848, Pasteur—who later elucidated the whole question of fermentation and became the father of the science of bacteriology—observed that ordinary tartaric acid rotates the polarized ray strongly to the right, but that certain tartars yielded an acid called racemic acid, identical with tartaric acid in every respect except that it was optically inactive. On further investigation he discovered that this racemic acid is a mixture of two kinds of tartaric acid in equal quantities and having equal but opposite effects on polarized light; and that the crystals of the dextro form and of the laevo form differ only as the right hand differs from the left or an object from its mirror-image. Pasteur also found that any organic optically active substance will yield two forms of crystal, left-handed and right-handed, and concluded that in such pairs of substances the arrangement of atoms must in one case be the inverse of the other. There the interpretation of the matter rested until 1874, when van't Hoff and Le Bel correlated the observations by the discovery that the molecule of an optically active organic compound contains at least one so-called asymmetric carbon atom—that is, a carbon atom linked to four different groups—showing that optical activity vanishes as soon as the carbon atom ceases to be asymmetric. This type of isomerism cannot be readily visualized through structural formulae written in one plane; but van't Hoff made it clear by picturing the carbon atom as a regular tetrahedron with linkages extending outwards from the four apices, and by using solid models to represent the compounds. On this basis it is apparent that a molecular structure comprising an asymmetric carbon atom may be either right- or left-handed and that there will be two such stereoisomers for each asymmetric carbon atom present; and the facts have been found to be in complete accordance with these deductions.

The phenomenon of optical activity and its interpretation on a stereo-chemical basis have proved of great usefulness, for it has been to the chemist a very powerful tool in ascertaining the constitution of many organic compounds. Particularly is this so in the case of the sugars which have the general empirical formula $C_6H_{12}O_6$. When Emil Fischer started systematic work upon the sugars, in 1883, practically nothing was known as to their constitution; in 1908, when his collected papers on sugar were published, the complex relationships had been resolved. Fischer had succeeded in determining the structural formula, and in synthesizing, each of the important sugars; he had prepared many of the possible stereoisomers, thereby confirming the usefulness of van't Hoff's theory, and had, indeed, systematized the whole matter. This is only one of his great achievements; for he had simultaneously established the constitution of many compounds of the so-called purin group, a group which includes substances such as caffeine and uric acid. His work on sugars brought in its train the necessity for examining further the nature and properties of substances which bring about the process of fermentation; from this it is but a short step to the proteins, a class of substances more directly connected with life processes than any other. And in this field likewise, which at the outset presented unparalleled difficulties, Fischer progressed a long way; he was able to break down the complex substances into simpler amino-acids and other nitrogenous compounds, to ascertain the structure of these decomposition products, and by bringing about recombination of these units to prepare synthetic peptides which approximate to the natural products.

The measure of Fischer's achievement in this matter is brought out by a quotation from a short history of chemistry published as recently as 1899:[12]

> Not only the simple formic and acetic acids, but complex vegetable acids, such as tartaric, citric, salicylic, gallic, cinnamic; not marsh gas and ethylic alcohol only, but phenols, indigo, alizarin, sugars, and even alkaloids identical with those extracted from the tissues of plants, are now producible by purely chemical processes in the laboratory. It might appear that such triumphs would justify anticipations of still greater advances, by which it might become possible to penetrate into the citadel of life itself. Nevertheless the warning that a limit, though distant yet, is certainly set in this direction to the powers of man, appears to be as justifiable now, and even as necessary, as in the days when all these definite organic compounds were supposed to be producible only through the agency of a "vital force." Never yet has any compound approaching the character and composition of albumen or any proteid been formed by artificial methods, and it is at least improbable that it ever will be without the assistance of living organisms.

This illustrates again the danger of prophecies as to the limitation of man's powers; for the limitations set are continually being transcended by the genius, and he would be rash who would now set a limit to what may be learned from biochemical investigations, in view of the extraordinary progress made within the present century; but to discuss this fascinating subject is beyond the scope of this sketch of the development of the principles of chemistry.

General and Inorganic Chemistry Since 1860

Compared with the enormous growth of organic chemistry, that of inorganic chemistry was for a long time insignificant. It remained for many years largely in the hands of the so-called practical man, who has been defined as the man who practices the errors of his grandfather; and contented itself largely with descriptions of substances rather than with their interrelations and structure. As one instance among many, it may be mentioned that there has been no real technical improvement in the Chamber Process of making sulphuric acid—which is the key substance, made by the millions of tons yearly, in all chemical manufacture—since Gay-Lussac invented his absorption tower nearly one hundred years ago; nor does this mean that there is no room for improvement, but merely that it was not *sought properly.* Indeed as late as 1900, many chemists considered that but little more, and that *little* not of the first importance, remained to be done in inorganic chemistry; the truth being the exact opposite—that we had then barely scratched the surface of this enormous field. It had not been adequately recognized that chemistry had been dealing in the main with the behavior of a rather restricted range of substances over a narrow range of temperature (say, from somewhat below the freezing point up to 400°) and, practically, at a single pressure—with a mere slice of the whole field, in fact—and that these conditions are quite arbitrary when we consider the whole subject-matter of chemistry.

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[12] W. T. Tilden, "A Short History of the Progress of Scientific Chemistry," p. 154.

Nor is the development of inorganic chemistry of subsidiary importance, from any point of view. If judged with respect solely to the monetary value of its products it would be far ahead of organic chemistry, as will be obvious if we recall that it is concerned with the production of all our metals, of building materials such as brick, cement, glass, and with the manufacture of all kinds of articles in every-day use. One reason for its comparative neglect for so many years is that inorganic chemistry is in a sense the more difficult in that, whereas organic compounds usually stay put and behave regularly—one might say that organic radicles are conservative and conventional—the behavior of many inorganic compounds is more complex, somewhat analogous to that of Dr. Jekyll and Mr. Hyde; another is that the great successes of organic chemistry attracted a majority of the workers. But the main reason is that the proper theories for the interpretation of the phenomena had not been available, consequently proper tools and adequate methods of investigation had not been developed.

The fundamental idea which was lacking is the conception of chemical equilibrium, the importance of which was not really grasped until about thirty years ago and is not yet adequately apprehended by many chemists. The first contribution to this question we need notice dates from 1865, when Guldberg and Waage published the so-called law of mass-action. This paper may be said to inaugurate the quantitative study of chemical equilibrium, though progress for many years was quite slow. Indeed at that time the conception of equilibrium was very recent; of the few cases then known, the majority were certain gases which had been observed to expand with rise in temperature in an apparently anomalous manner as compared to the so-called permanent gases; this anomaly was accounted for on the basis that a progressive dissociation of the gas, e. g. ammonium chloride (NH_4Cl) into simpler molecules of ammonia (NH_3) and hydrochloric acid (HCl), takes place on heating and that the constituents recombine on subsequent cooling. Hundreds of instances are now known, all of which are in quantitative accord with the law of mass-action.

According to this law, the extent of chemical action within a homogeneous gaseous system is determined by the "active mass",—or better, the effective concentration—of each species of molecule taking part in the reaction; this implies that an apparently stationary condition, a state of equilibrium, is finally reached, at which point the tendency of the reaction to go forward is just counterbalanced by the tendency of the reverse reaction. This may be made more objective by an actual example. By the equation

$$\begin{array}{ccccccc} \mathrm{CO} & + & \mathrm{H_2O} & \rightleftharpoons & \mathrm{H_2} & + & \mathrm{CO_2} \\ \text{carbon monoxide} & & \text{steam} & & \text{hydrogen} & & \text{carbon dioxide} \end{array}$$

we symbolize the fact that under appropriate conditions in any mixture of the gases CO and H_2O some proportion of the gases H_2 and CO_2 will be formed, and conversely, in any mixture of H_2 and CO_2 some proportion of CO and H_2O will be formed; and the law of mass-action states that the concentrations of the several gases will always adjust themselves so that ultimately

$$\frac{[\mathrm{H_2}]\ [\mathrm{CO_2}]}{[\mathrm{CO}\ ]\ [\mathrm{H_2O}]} = \mathrm{K}$$

where the symbols $[H_2]$, etc., denote the concentrations of the several reacting species, and K is a constant, the equilibrium constant, the value of which depends upon the temperature but not upon the original amounts of any of the substances. From this it is obvious that, if we know the value of K corresponding to any temperature, we are in position to predict exactly what will happen in any mixture in which this reaction may take place, and consequently to select the conditions under which the maximum yield of any one of the substances may be expected. The usefulness of this is so apparent as to require no comment.

The law of mass-action is but a special case of the general question of equilibrium treated so comprehensively by Willard Gibbs, at that time Professor of Mathematical Physics at Yale, on the general basis of the laws of thermodynamics. These two laws now underlie so much of the reasoning upon which advances in chemistry and physics have been based that we must go back a little to consider them.

The doctrine that heat is an imponderable became finally untenable about 1860, when the work of Mayer in Germany and of Joule in England had finally convinced everybody that heat is a form of energy, and that heat and work are quantitatively interchangeable. This leads directly to the First Law of Thermodynamics, the doctrine of the conservation of energy, that energy is indestructible and uncreatable, that energy, though apparently disappearing, is simultaneously reappearing in another form. The second law in its briefest form is that a thermodynamic perpetual motion is impossible; perhaps I can best convey an idea of it by means of the picturesque analogies of a recent writer:[13]

> There is one law that regulates all animate and inanimate things. It is formulated in various ways, for instance: Running down hill is easy. In Latin it reads, *facilis descensus Averni*. Herbert Spencer calls it the dissolution of definite coherent heterogeneity into indefinite incoherent homo-

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[13] Slosson, Creative Chemistry, page 145.

> geneity. Mother Goose expresses it in the fable of Humpty Dumpty, and the business man extracts the moral as, "You can't unscramble an egg." The theologian calls it the dogma of natural depravity. The physicist calls it the second law of thermodynamics. Clausius formulates it as "The entropy of the world tends toward a maximum." It is easier to smash up than to build up. Children find that this is true of their toys; the Bolsheviki have found that it is true of a civilization.

These two laws, which had been established largely by the work of Mayer, Joule, Clausius and William Thomson (later Lord Kelvin), have only been confirmed by all subsequent work; and they are now considered as fundamental as any laws in physical science. The great advance in applying them generally to chemical processes is due to Gibbs, who in 1876 and 1878 printed in the Transactions of the Connecticut Academy the two parts of his epoch-making paper "On the Equilibrium of Heterogeneous Substances." Gibbs was, however, so far in advance of his time and his paper was moreover so inaccessible, that the importance of his work was not recognized for ten years, when it was proclaimed by Roozeboom and began to be used as a guide—almost entirely by Hollanders and Germans—in the interpretation of chemical phenomena. It is hardly too much to say that the very large number of subsequent advances in this field are merely applications and variations of Gibbs' fundamental considerations; that his paper mapped out the lines of advance in a new field of chemical science comparable in importance to that uncovered by Lavoisier. The conception of equilibrium in chemical processes constitutes the central idea of what is commonly called physical chemistry, which however would be better termed theoretical or general chemistry since it deals with the general principles of the science.

To many Gibbs' name is familiar only as the formulator of the phase rule, a general principle, derived from his thermodynamic discussion of chemical equilibrium, which enables one to sort chemical systems tending to equilibrium into categories, and to state qualitatively what behavior may be expected in each type of system. The phase rule has been of indispensable service in the elucidation of problems as apparently diverse as the constitution of alloys (another large field in which we have done little more than scratch the surface hitherto); the origin of salt-deposits in the earth; the separation of potash or other valuable salts from the waters of saline lakes; the relation between different crystal forms of the same chemical substance, as exemplified in many minerals and in the so-called allotropic modifications of the elements themselves (e. g. diamond and graphite; phosphorus, white and red, etc.). Indeed the service which these doctrines with respect to chemical equilibrium have rendered is but a fraction of what they will render to chemical science, and hence to the people at large.

For a long time there had been investigations looking towards a relation between physical properties and chemical constitution. An early instance is the work of Dulong and Petit, who discovered that equal amounts of heat are required to raise equally the temperature of solid and liquid elements, provided quantities are taken proportional to the atomic weights; and this was frequently used as a criterion in fixing upon the proper atomic weight. This is an instance of the necessity of comparing quantities which are really comparable chemically, instead of equal weights; that regularities which otherwise would remain hidden will be apparent when an equal number of chemical units —molecules—are considered. Hence it is obvious that few such regularities would be observed so long as there was confusion with respect to atoms and molecules; but since 1860 there has been continuous progress in this direction, though until very recently chemists had in their comparisons often made insufficient use of chemical units, as compared with the arbitrary unit of weight, the gram. As examples of this type of relationship we may mention: the heat capacities (specific heats) of gases; the molecular volume, the heat-change accompanying combustion, formation, or melting, particularly as applied to homologous series of organic compounds; the relation between constitution and color and other optical properties, etc.

Along with this went naturally the question of the properties of a substance as affected by mixture with another, of solutions in particular. The fact that the boiling-point of a solution is higher than that of the solvent itself had long been known, and measurements of the rise in boiling point caused by equal weights of dissolved material had been made; but it was not until 1884 that Ostwald pointed out that this rise is approximately the same, for any one solvent, when computed for equal numbers of molecules dissolved in the same amount of the solvent. The measurements had been mainly of solutions of a salt in water; but in 1886 Raoult extended the observations to other substances and stated what is now known as Raoult's law, which may be considered as the fundamental law formulating the dependence of the general properties of a perfect solution upon its composition; namely, the lowering of the vapor pressure of the solvent is proportional to the number of dissolved molecules per unit of solvent, or as now frequently phrased, the partial pressure of a component of a solution is proportional to its molar fraction, the molar fraction being defined as the ratio of the number of molecules of that component to the total number of molecules present. Soon thereafter van't Hoff gave the thermodynamic relationships between lowering of vapor pressure and raising of boiling-point, lowering of freezing-point, and osmotic pressure; by means of which any one of these may be deduced from another provided that certain constants characteristic of the solvent are known. It was then possible, from such measurements, to calculate the molecular weight of the substance in solution; when this was done, many of the results were anomalous—in particular, the apparent molecular weight of a salt in solution in water was little more than half what one would expect from its formula.

Now it had long been known that certain classes of substances dissolved in water yield a solution which is a good conductor of electricity, and that aqueous solutions of other substances are poor conductors; the former class, called electrolytes by Faraday, comprises salts, acids and bases (alkalies), whereas the typical non-electrolyte is an organic substance such as sugar. And it was precisely these electrolytes which exhibited the anomalous molecular weight. To account for this anomaly Arrhenius propounded the theory of electrolytic dissociation, the basic idea of which is that the electrolytes, when dissolved in water, dissociate into two or more constituent particles, that these constituents are the ions, or carriers of electricity through the solution, and that each ion affects the general properties of the solution just as if it were an independent molecule. This theory is another landmark in the field of chemistry, for it has served to correlate and systematize a very large number of apparently diverse facts.

It would lead too far to go into the consequences and applications of the theory of ionization; how it enables us to choose the optimum conditions under which to carry out many analytical operations; how it leads to the view that acidity is determined by the actual concentration of hydrogen-ion (H^+), and basicity (alkalinity) by hydroxyl-ion (OH^-), etc. Its usefulness and importance in aiding us towards a real knowledge of aqueous solutions—a knowledge so essential to progress in many lines—is so great as to require no emphasis. And yet the theory is not completely satisfactory, there being still some outstanding anomalies, particularly in connection with the so-called strong electrolytes as typified by ordinary salts; but there is hope that these discrepancies will disappear with the growth of knowledge of electrochemistry.

The fundamental law of electrochemistry was discovered by Faraday prior to 1840, namely: that one unit of electricity transports one chemical equivalent of an ion, irrespective of voltage, temperature, concentration or other conditions. Later, it was established that these ions move independently of one another, and with characteristic velocities, facts which, with others, were satisfactorily coordinated by the theory of ionization; which in turn led to greatly improved control of practical electrochemical processes, such as electroplating. Again, it had long been known that an electromotive force is set up whenever there is a difference of any kind at two electrodes immersed in an electrolyte, and when two similar electrodes are placed in different solutions, or in solutions of the same substance at different concentrations. The next step in advance was taken by Nernst, in 1889, who, from thermodynamical reasoning confirmed by direct experiment, deduced the relation between the electro-motive force and the ratio of effective concentration of the active ion in one solution to that in the other. Measurement of electromotive force, therefore, under appropriate conditions, yields independent information as to the effective concentration, or activity, of the ions. Nor is this the only application of this principle to the development of chemistry; for it also affords a measure of chemical affinity.

One of the characteristic phenomena accompanying a chemical change is an evolution or absorption of heat; in other words, the amount of heat contained by the reacting system changes with the chemical change. The measurement of this heat change, which may range from a large negative quantity through zero to a large positive quantity, is the province of thermo-chemistry. Our knowledge of these heats of reaction is largely due to Thomsen and to Berthelot, each of whom started from the supposition that the heat effect is a direct measure of relative affinity; and it was with this end in view that they carried out the very laborious work involved in these determinations. It is now clear that this supposition is erroneous, that the maximum work producible by a reaction, or its free energy, is a truer measure of affinity, the heat effect being an important factor in this maximum work or free energy. The systematic determination of the free energy of reactions, one of the most potent methods being the electrical method outlined above, is an outstanding task of modern chemistry, of consequence to the progress of the science as well as to industrial progress.

Graham, the discoverer in 1829 of the law relating the rate of diffusion of a gas to its density, later made experiments on the rate of diffusion of dissolved substances through animal membranes; this work led him to divide substances into two categories—the rapidly moving crystalloids, typified by salt, and the slow moving colloids, typified by gum arabic or gelatine. For a long time this distinction persisted, colloids being regarded as somewhat mysterious, rather messy, substances; and it was apparently considered a good explanation of some ill-understood phenomenon to attribute it, if possible, to a colloid. This whole matter received little systematic attention for forty years and only after 1900 did it become evident that we should not speak of a colloid as a distinct class of substances, but may speak only of the colloidal state. The characteristic phenomenon is the dispersion of one substance in another, the system being therefore heterogeneous; and the properties of the colloidal system depend upon the kind of particle, and upon their fineness,—in short, upon the nature and extent of the surface of separation of the two phases. In an outline on the present scale one cannot go further into colloid chemistry, except to say that nearly everything remains to be done and that increased knowledge of the subject is fundamental to progress along many lines in biology and medicine, and is also of inestimable importance to all manner of industries, ranging from tanning to pottery.

Closely connected with this, since they also are surface effects, are the phenomena of adsorption and of catalysis, both known in more or less isolated instances for a long time, and both very ill understood. Their importance has been demonstrated recently, the former in connection with the provision of a satisfactory gas-mask, the latter as a means of making certain products—for instance, edible fats out of inedible oils,—in the fixation of atmospheric nitrogen, etc. And there is no question that both phenomena will be made use of increasingly, and that this increase will be accelerated as soon as we begin to understand the principles underlying these phenomena, a matter upon which we are still in the dark. Indeed, even as it is, extension of the use of catalytic methods is proceeding so rapidly that predictions are being made that we are entering upon what might be called a catalytic age in so far as the making of many chemical products is concerned.

As we have already noted, practically all chemical work, until very recently, had been carried out within a temperature range extending only from 0° up to 400° and at pressures ranging from atmospheric down to, say, 0.01 atmosphere. But the recent extension of these ranges has had so many practical consequences as to require some mention. This extension, though it hardly involves any important new chemical principle, has in a sense been equivalent to one, in that it has forced chemists to consider the subject more broadly and to remember that "ordinary conditions" are quite arbitrary in reference to the subject as a whole. To illustrate, the chemistry at the 1000° horizon, though subject to the same general principles, has to deal with only a small fraction of the compounds familiar to us at the 25° horizon, and is incomparably simpler; at the 2000° horizon it would be still simpler, and at still higher temperatures—as in many of the stars —the elements, at that temperature all gaseous, in place of being combined with one another, would probably be in part themselves dissociating.

Before 1845 Faraday had succeeded in liquefying, by cooling and compressing, many of the gases then known; but a few of the most common gases—viz., nitrogen, oxygen, hydrogen, carbon monoxide, nitric oxide, methane—resisted all his efforts, wherefore they were often alluded to as the "permanent gases." The clue was given in 1861 by Andrews, who showed that there is for each gas a critical temperature above which it cannot be liquefied by any pressure whatever;[14] and the reason for lack of success with the permanent gases was that the lowest temperature employed had been above the critical point of those gases. With appreciation of this point and with improvements of technique, resulting in part from theory and in part from practice, success was finally achieved in all cases; all known gases have therefore now been liquefied, and there is only a difference in degree of "permanence" between hydrogen which condenses to liquid at 30° absolute and water vapor (steam) which condenses at 373° absolute. The main victories in conquering this region are given in the following table:

LIQUEFACTION OF THE "PERMANENT" GASES

Substance	Date when liquid first obtained	Observer		Liquid				
			Critical Temperature		Boiling Temperature		Freez'g Temp.	
			C.	abs.	C.	abs.	C.	abs.
Oxygen	1883	Wroblewski	—118°	155	—181°	92	—235	38
Nitrogen	1883	Wroblewski	—146	127	—195	78	—215	58
Hydrogen	1898	Dewar	—243	30	—252	21	—248	17
Helium	1908	Onnes	—268	5	—269	4		2.5

To this may be added that liquid air was first obtained by Wroblewski in 1885, was available for research purposes in 1891, and since 1895, with the development of the commercial machine for producing it, has become an industry; it is now indispensable to several lines of work—for instance, wherever very low pressures are required. Incidentally, too, its development resulted in the invention of the vacuum-jacketed, or Dewar, tube which is now a necessary tool in all work at low temperatures and a convenience to the community generally.

With the command of low temperatures, it is now possible to make accurate measurement, e. g. of specific heats, at temperatures not so far removed from the absolute zero. And there is reason to believe that this type of work is going to furnish very valuable information on some moot questions; for instance, on the entropy of substances at the lowest temperatures and on the applicability of the Nernst heat theorem, called by some the third law of thermodynamics—questions which bear a very intimate relation to the problem of the nature of chemical affinity.

Apart from mainly qualitative work, such as that of Moissan with his arc-furnace on the carbides, little accurate high-temperature work was done until about 1900. In the meantime methods of control and measurement have been developed to such an extent that many types of measurement may be made just as accurately at 1000° as at 100°. This has enabled many equilibria, both homogeneous (usually in gas systems) and heterogeneous (that is, essentially solubilities), to be determined carefully over a wide range of temperature. Such knowledge is essential for many purposes, both practical and theoretical—from the nature of combustion to the constitution of alloys and the mode of formation of minerals and rocks. Very recently high tem-

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[14] Though, as we now know, it may be solidified by application of sufficient pressure at temperatures higher than the critical end-point of the liquid.

peratures have been coupled with minimal pressures in experimental work on electron emission and related topics; but this is at the moment usually considered a part of the domain of physics, which has not yet received adequate attention from a chemical point of view. In the field of high pressures, as in that of high temperatures, recent technical progress has made it possible to follow many types of changes with as high accuracy at a pressure of 10,000 atmospheres (i. e. 150,000 pounds to the square inch) as at 10 atmospheres. This is bringing to light phenomena hitherto unsuspected; thus, when the whole range is considered, it appears to be the rule, rather than the exception, that a substance when solidified exists in more than one crystalline form, each stable within a definite range of temperature and pressure. As an instance of this, there are in addition to ordinary ice, at least four other forms of crystalline water, stable at high pressure; and under increasing high pressure the freezing temperature of water steadily rises until at, for instance, a pressure of 20,000 atm. it freezes about 73° (centigrade) higher than its ordinary freezing point.

The phenomena observed at high and low temperatures and at high and low pressures all illustrate the fact that chemistry should not be looked upon as a collection of isolated things which can be manipulated in a sort of magical way, but is to be thought of as, in a sense, almost a continuum all parts of which are subject to definite laws, still incompletely elucidated; the relative behavior of all substances being controlled by these laws in the same sense as the relative motions of the heavenly bodies are controlled by the law of gravitation.

In this brief sketch of the development of chemical science, many things must remain unmentioned. Yet it must not be supposed that these things are intrinsically unimportant; indeed an explanation of some puzzling phenomenon may arise out of work in another field, apparently entirely unrelated, each advance in knowledge of any field being that much wrested from the domain of ignorance, and reacting in favor of advances at other points of the line. In particular it has not been practicable to mention the several branches of applied chemistry, for instance, the study of the substances and reactions involved in life-processes, with its remarkable advance within the last few years, which would require a chapter to itself; or even analytical chemistry, an essential branch of the subject, which develops with each development of principle, and is to be regarded as including all methods of analysis and not merely the semi-traditional methods applied to a somewhat restricted group of salts of certain metallic bases. The growth of the whole subject-matter may perhaps be gauged from the fact that the 1920 volume of Chemical Abstracts, which gives merely brief abstracts of papers of interest to chemists published within the year, contains more than 4,000 pages, and that the index to this volume alone will cover more than 600 pages closely printed in double column. From this it is obvious that, even though a large proportion of these papers contain little of real value, one cannot keep abreast of advances in the whole subject but can only hope to have a general knowledge of principles and to acquire a special knowledge of some restricted field.

These principles of chemical science are of its essence and constitute its philosophy; only with development of this philosophy will it be possible to progress in the correlation and systematization of the multitudinous facts of chemistry. The progress of this philosophy, which indeed demands the services of the physicist as much as those of the chemist, is obliterating the line of demarcation between these two sciences. Initially physics dealt mainly with changes which affect matter independently of its composition, whereas chemistry was concerned mainly with the change of composition; but the physicist and chemist came to meet on common ground for the reason that the quantitative measures of most of the so-called physical properties are intimately connected with the constitution of the substance. And it may be said that the recent very significant advances—dating, say from the discovery of the X-rays—concern the chemist just as much as the physicist, and that each of them should be conversant with the general mode of thought of the other. Indeed the several sciences have in the past been too far apart from one another, and we should now seek increased co-operation, for it is precisely in the boundary regions between them that the most valuable advances in the immediate future will be made.